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**(54) Improvements in or relating to
flame retarded claddings**

**(57) A heat-recoverable flame
retarded cladding is formed from a
polymeric composition comprising a
substantially cross-linked blend of a
vinyl acetate/alkene copolymer with a
thermoplastic polyalkene or
thermoplastic alkene/alkene**

copolymer and incorporates an
effective amount of a halogen-free
inorganic flame retardant. The blend
contains at least 66 weight percent
vinyl acetate alkene copolymer and
the vinyl acetate/alkene copolymer
has a vinyl acetate content of greater
than 40 weight percent.

The claddings are characterised by
low flammability and inertness to
chemical solvents such as oils.

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SPECIFICATION

Improvements in or relating to flame retarded claddings

The present invention relates to cladding for elongate substrates.

Accordingly, the present invention provides a heat recoverable flame retarded cladding formed from a polymeric composition which comprises a substantially cross-linked blend of a vinyl acetate/alkene copolymer with a thermoplastic polyalkene or thermoplastic alkene/alkene copolymer and incorporates an effective amount of a halogen-free inorganic flame retardant, the blend containing at least 66 weight percent vinyl acetate/alkene copolymer and the vinyl acetate alkene copolymer having a vinyl acetate content of greater than 40 weight percent.

The alkene component of the vinyl acetate alkene copolymer and the polyalkene, when present, preferably comprises a C_2-C_8 alkene, particularly an α -unsaturated alkene such as ethylene, 1-propylene and 1-butene and particularly ethylene. Alkene/alkene copolymers which may be employed in the compositions of the invention are preferably C_2-C_8 alkene/ C_2-C_{12} alkene copolymers, particularly ethylene copolymers with C_3-C_{12} alkenes, especially α -unsaturated C_3-C_{12} such as *n*-propyl-1-ene, *n*-but-1-ene, *n*-pent-1-ene and *n*-hex-1-1. Particularly preferred ethylene copolymers contain greater than 50 weight per cent, for example greater than 60 weight per cent, more preferably greater than 70 weight per cent, for example greater than 85 weight per cent, ethylene. Of particular interest are the so-called linear low density ethylene copolymers having a density in the range 0.910 to 0.940 gm/cm³ at 25°C described in UK Patent Application No. 7,911,916 and Canadian Patent No. 873,828.

Preferably the vinyl acetate content of the vinyl acetate/alkene copolymer is in the range 45 to 98 weight per cent, particularly greater than 55 weight per cent, e.g. up to 95 weight per cent, especially 65 to 95 weight per cent, e.g. 65 to 90 weight per cent and more especially 65 to 85 weight per cent, for example 70 to 80 weight per cent. Additionally or alternatively, the weight ratio of vinyl acetate/alkene copolymer to the polyalkene or alkene/alkene copolymer blend component preferably ranges up to 1:0.2.

Additionally or alternatively, it is preferred that the overall amount of vinyl acetate in the blend is at least 30 weight per cent, particularly greater than 40 weight per cent, e.g. in the range 65 to 75 weight per cent.

Under most circumstances, it may be desirable that the polymeric composition include a coupling agent to improve the compatibility of the flame retardant with the polymer component(s) of the composition, e.g. to improve the physical properties of the composition. Preferred coupling agents include organo-silicon and titanium derivatives such as silanes and titanates.

As examples of silanes may be mentioned dimethyl-dichlorosilane, methyl trichlorosilane, vinyl trichlorosilane, γ -methacryl-oxypropyl-trimethoxysilane, N,N-bis (β -hydroxyethyl)- γ -amine-propyl-triethoxy silane, vinyl propyl-trimethoxysilane, γ -methacrylox-propyl-trimethoxy silane, γ -mercaptopropyl-trimethoxy silane, vinyl trimethoxy silane, γ -glycidoxy propyl trimethoxysilane, β -(3,4-epoxy-cyclohexyl) ethyl trimethyl silane and vinyl trimethoxyethoxysilane. Further appropriate silanes are exemplified in UK Patent No. 1,284,082.

As examples of titanates and other organo-titanium derivatives useful as coupling agents may be mentioned tetraisooctyl titanate, isopropyl diisostearyl methacryl titanate, isopropyl-triisostearoyl titanate, isopropyl-triacryl titanate, titanium di-(dioctyl pyrophosphate) and especially the so-called hybrid titanates such as isopropyl dimethacryl isostearoyl titanate. Additional suitable titanium compounds are described in S. J. Monte & G. Sugerman, J. Elastomers & Plastics Volume 8 (1976) pages 30-49, and in Bulletins KR 0376-4 and 0278-7 "Ken-React Titanate Coupling Agents for Filled Polymers" published by Kenrich Petrochem Inc.

The weight ratio of coupling agent, when employed, to fire retardant preferably lies in the range 0.005 to 0.1:1 respectively, more preferably 0.01 to 0.05:1 respectively.

The preferred flame retardants are those that release water on heating, particularly hydrated aluminium oxides of the formula $Al_2O_3 \cdot xH_2O$ wherein *x* lies in the range 0.5 to 3 especially $Al_2O_3 \cdot 3H_2O$, ammonium or sodium dawsonite, hydrated magnesia and hydrated calcium silicate, especially α -alumina trihydrates. Flame retardants such as alumina trihydrate preferably have a specific surface area of at least 0.1 m²/g, desirably at least 1 m²/g, e.g. 1 to 80 m²/g, especially 3 to 20 m²/g, as measured by the Brunauer, Emmett and Teller (BET) nitrogen absorption method.

The particle size of the flame retardant is preferably less than 5 microns, and most preferably less than 2 microns. Alternatively or additionally, it may be advantageous to employ a flame retardant comprising a blend of different particle sizes, for example to reduce the melt viscosity of the composition. If desired, the flame retardant may be chemically treated, to improve its compatibility with the polymeric material, with one of the above mentioned coupling agents, or, in the case of certain flame retardants such as alumina trihydrate, with processing aids such as stearic acid or stearates e.g. calcium stearate.

The flame retardant is preferably used in an amount by weight of from 10 to 400 parts thereof per 100 parts of the polymeric component(s), most preferably from 50 to 200 parts per 100 parts of

the polymeric component(s). Notable results have been obtained using an amount of from 80 to 150 parts by weight of the flame retardant per 100 parts of the polymeric component.

Apart from the flame retardant the compositions used in the cladding of present invention may comprise additional additives, for example fillers, stabilisers such as ultra-violet stabilisers, antioxidants, acid acceptors and anti-hydrolysis stabilisers, foaming agents and colourants, processing aids such as plasticizers, or additional polymers. If additional additives are employed, then it is preferred that the compositions contain less than 5 weight per cent halogen in the composition as a whole and more preferably less than 2 weight per cent halogen and particularly contain no halogen.

The polymeric compositions may be produced in conventional manner, for example by blending the components thereof in a Banbury mixer. They may then be processed into cladding form, for example by extrusion or moulding depending on the nature of the cladding and substrate, and simultaneously or subsequently cross-linked.

The polymeric composition may be cross-linked, for example, by the incorporation of a cross-linking agent or by exposure to high energy radiation. Suitable cross-linking agents are free radical initiators such as peroxides for example, 2,5-bis (t-butyl peroxy)-2,5-dimethylhexane and α,α -bis (t-butyl-peroxy)-di-isopropylbenzene. In a typical chemically cross-linkable composition there will be about 0.5 to 5 weight per cent of peroxide based on the weight of the polymeric blend. The cross-linking agent may be employed alone or in association with a co-curing agent such as a poly-functional vinyl or allyl compound, e.g. triallyl cyanurate, triallyl isocyanurate or pentaerythritol tetramethacrylate.

Radiation cross-linking may be effected by exposure to high energy irradiation such as an electron beam or γ -rays. Radiation dosages in the range 2 to 80 Mrads, preferably 2 to 50 Mrads, e.g. 2 to 20 Mrads and particularly 4 to 12 Mrads are in general appropriate. For the purpose of promoting cross-linking during irradiation, preferably from 0.2 to 5 weight per cent of a prorad such as a poly-functional vinyl or allyl compound, for example, triallyl cyanurate, triallyl isocyanurate or pentaerythritol tetramethacrylate are incorporated into the composition prior to irradiation.

The degree of cross-linking of the compositions may be expressed in terms of the gel content (ANSI/ASTM D2765-68) of the cross-linked polymeric composition, i.e. excluding non-polymeric additives that may be present. Preferably the gel content of the cross-linked composition is at least 10%, more preferably at least 20%, e.g. at least 30% more preferably at least 40%.

The claddings according to the invention are in dimensionally recoverable form, that is to say, in a form such that the dimensional configuration thereof may be made substantially to change when subjected to appropriate treatment, especially heat-recoverable form, the dimensional configuration of which may be made substantially to change when subjected to heat. The cladding may be rendered heat-recoverable by deformation of the heat-stable configuration thereof in cross-linked form at an appropriate elevated temperature, e.g. at a temperature above the crystalline melting point or softening point of the polymeric composition with subsequent cooling whilst in the deformed configuration, in manner known *per se*, for example as described in US Patents 2,027,962, 3,086,242 and 3,957,372.

In addition and under certain circumstances, it may be desirable to coat at least a part of the surface of the cladding which is to contact the substrate with a sealant or adhesive, e.g. a hot-melt, heat activatable, pressure sensitive or contact adhesive or a mastic, particularly with a hot-melt adhesive such as disclosed in W. German Offenlegungsschrift 2,723,116.

One aspect of the present invention of particular interest concerns electrical insulation where extremely stringent non-flammability requirements exist. Examples of the application of the present invention to electrical insulation are cable jackets and wire and cable harness conduits, where the cladding is applied over the length of the substrate, and wire and cable splice covers and terminations in sleeve form, and cable and harness break-outs in the form of or moulded components e.g. udders (often referred to as boots), where the cladding is applied only to a section of the length of the wire, cable or harness system.

A further aspect of the present invention of particular interest concerns the sealing or mechanical or environmental protection of pipes or ducts or at least sections thereof, e.g. joints or damaged regions, e.g. in utility supply systems such as gas or water pipes, district heating pipes, ventilation and heating ducts, and conduits or pipes carrying domestic or industrial effluent. One important example of such application is in the jointing of air conditioning or ventilation ducts where the cladding may be employed in the form of a sleeve encompassing the joint in heat-recoverable form.

In the above mentioned uses, the claddings in accordance with the invention are characterised by notably low flammability and low smoke and corrosive gas emission under rigorous flammability conditions. Such low flammability characteristics have been found to be directly attributable to the overall level of vinyl acetate in the copolymer of the composition. Further, when compared to analogous compositions having no polyalkene or alkene/alkene copolymer blend component and the same level of the vinyl acetate content, claddings formed from compositions including a polyalkene or alkene/alkene blend component are also found to possess a substantial improvement in their inertness to chemical solvents particularly to oils, their flame retardancy and often their smoke emission under rigorous flammability conditions.

Compositions suitable for the production of claddings according to the invention are illustrated by the accompanying Examples, wherein parts and percentages are by weight:

Examples 1 and 2

The relevant composition set out in Table 1 below which shows the parts (approximated to the nearest whole number) of the various constituents, were uniformly blended on a two roll laboratory mill heated to a temperature of 120 to 140°C, compression moulded into plaques at 190°C and then irradiated under atmospheric conditions with a 5.8 MEV electron beam at the radiation dosages indicated. Samples were subjected to the Test Methods set out below.

Examples 3 and 4 (comparative)

The present compositions set out in Table 1 were blended in analogous manner to that described in the preceding Examples, the two roll laboratory mill being cooled to prevent sticking and plaques produced therefrom for comparison purposes in the following tests.

Table 1

			Comparative	
Example No.	1	2	3	4
DYNH 3 (trade name) low density polyethylene ex Union Carbide	0	17	0	0
Sclair 11-D-1 (trade name) low density polyethylene ex Dupont	17	0	0	0
Vynathene EY-907 (trade name) 60% weight vinyl acetate-ethylene copolymer ex USI	33	33	0	0
Vynathene EY-902 (trade name) 40% weight vinyl acetate-ethylene copolymer ex USI	0	0	40	50
Alumina Trihydrate (silane coated) Hydral 705 (trade name)—available from Alcoa Corp. coated with 1.5% vinyltrimethoxyethoxysilane	50	50	60	60
Radiation dosage (Mrads)	6	12	12	12

Test Methods

The plaques produced in accordance with the preceding Examples were subjected to the following tests.

Water resistance measured as % water uptake	ASTM-D-570—77 except that sample disc 25 mm in diameter and 1.5 mm in thickness is employed.
Oil resistance measured as % oil uptake	ASTM-D-570—77 except that sample disc 25 mm in diameter and 1.5 mm in thickness is employed.
Tensile strength	BS 903 part A2
Elongation	BS 903 part A2
Flammability measured as limiting oxygen index	ASTM-D-2863
Smoke emission	measured in an Aminco NBS smoke chamber, in accordance with the Aminco-NBS smoke density chamber catalogue No. J4-5800B, J4-5800BE, instruction 1410 published Nov. 1975 by American Instrument Co. 8030 Georgia Ave. Silver Spring, Maryland 20910.

The results are set out in Table 2 below and clearly demonstrate *inter alia* the improved oil resistance of the blends (Example 1 and 2) when compared to the copolymer in the absence of blend polyethylene component (Examples 3 and 4), having the same ethylene and vinyl acetate content as the blend, as well as improved flame retardancy and in the majority of cases lower smoke emission.

Table 2

Table 2			Comparative		
	Example No.	1	2	3	4
5	% Water uptake @ 90°C 24h	9.0	7.3	8.0	15.4
	48h	13.4	11.4	12.5	18.2
	% Oil uptake @ 100°C ASTM No. 2 (Mineral Oil)	13	13	54	42
10	Synthetic lubricating Oil British Spec. D. Eng. R. D. 2487	33	29	80	77
	Tensile strength (MPa)	12.1	11.2	12.0	13.5
	Elongation (%)	230	102	200	240
	Oxygen index (%O ₂)	29.0	30.0	34.0	27.0
	T ₁₆ (min) Flaming Mode	8.5	9	10.5	1.5

15 **Example 5**

A heat-shrinkable tape was produced from the following formulation:

	Constituent	%	
	*Sclair 11D1	17	
	Vinyl acetate/ethylene copolymer containing 60% vinyl acetate	33	
20	Al ₂ O ₃ · 3H ₂ O coated with 1.5% of vinyl trimethoxyethoxy silane	50	20

*Sclair 11D1 is the Trade Name for a linear low density ethylene/butene copolymer commercially available from Dupont.

The constituents were compounded on a twin roll mill at 120 to 140°C, cooled and pelletised. The pellets so produced were fed to a conventional extruder fitted with a tape die, maintained at 25 140°C and extruded into tape 100 mm wide and 1.5 mm thick. The resulting tape was subsequently irradiated with high energy electrons to a total dose of 6 Mrads. 25

After irradiation, the tape was heated to 150°C, expanded lengthwise to 50% of its original length and allowed to cool in this expanded condition. Thereafter the tape was coated with a thin layer (0.5 mm) of a hot-melt adhesive of composition in accordance with W. German Offenlegungsschrift 30 2,723,116, Example 3, formulation "O". The physical properties of the tape prior to coating were as follows: 30

	Tensile strength (23°C)	12.0 MPa	
	Elongation at break (23°C)	266%	
	LOI (23°C)	29	
35	Tensile strength (150°C)	2.0 MPa	35
	Elongation at break (150°C)	105%	
	100% Tangent Modulus (150°C)	1.2 MPa	

The heat-shrinkable adhesive coated tape so produced was employed to seal the joint of a 150 mm diameter metal air conditioning duct by pre-heating the duct in the region of the joint, wrapping the tape around the duct over the joint region so that sequential turns of the tape partially overlap and heating the tape with a conventional propane gas torch, so causing the tape to shrink tightly around the joint and causing the adhesive to melt and form a strong adhesive bond between the cladding so formed and the duct substrate. 40

In a modification, the pelletised material is extruded in the form of a sleeve, which is then rendered radially heat-recoverable and coated with adhesive in analogous manner to that described 45

above. The sleeve so produced is then located above the duct joint and recovered by the application of heat.

Claims

1. A heat recoverable flame retarded cladding formed from a polymeric composition which comprises a substantially cross-linked blend of a vinyl acetate/alkene copolymer with a thermoplastic polyalkene or thermoplastic alkene/alkene copolymer and incorporates an effective amount of a halogen-free inorganic flame retardant, the blend containing at least 66 weight percent vinyl acetate/alkene copolymer and the vinyl acetate alkene copolymer having a vinyl acetate content of greater than 40 weight percent. 5
2. A cladding as claimed in claim 1, wherein the blend component is polyethylene or a thermoplastic ethylene/C₃—C₁₂ alkene copolymer. 10
3. A cladding as claimed in claim 2, wherein the blend component is an ethylene/C₃—C₁₂ alkene copolymer having a density in the range of from 0.910 to 0.940 g cm⁻³ at 25°C.
4. A cladding as claimed in any one of claims 1 to 3, wherein the overall amount of vinyl acetate in the blend is at least 30 weight percent. 15
5. A cladding as claimed in any one of claims 1 to 4, wherein at least part of one surface thereof is coated with sealant or adhesive.
6. A cladding as claimed in claim 5, wherein the coating is a hot-melt adhesive.
7. A heat recoverable flame retarded cladding formed from a composition substantially as described in Examples 1, 2 or 5 herein. 20

New claims or amendments to claims filed on 15 Nov 1982.

Superseded claims 1—7.

New or amended claims:—

1. A dimensionally recoverable hollow article formed from a polymeric composition which comprises a substantially cross-linked blend of a vinyl acetate/alkene copolymer with a thermoplastic polyalkene or thermoplastic alkene/alkene copolymer and incorporates an effective amount of a halogen-free inorganic flame retardant, the blend containing at least 66 weight percent vinyl acetate/alkene copolymer and the vinyl acetate alkene copolymer having a vinyl acetate content of greater than 40 weight percent. 25
2. An article as claimed in claim 1, wherein the blend component is polyethylene or a thermoplastic ethylene/C₃—C₁₂ alkene copolymer. 30
3. An article as claimed in claim 2, wherein the blend component is an ethylene/C₃—C₁₂ alkene copolymer having a density in the range of from 0.910 to 0.940 g cm⁻³ at 25°C.
4. An article as claimed in any one of claims 1 to 3, wherein the overall amount of vinyl acetate in the blend is at least 30 weight percent. 35
5. An article as claimed in any one of claims 1 to 4, wherein at least part of one surface thereof is coated with sealant or adhesive.
6. An article as claimed in claim 5, wherein the coating is a hot-melt adhesive.
7. An article as claimed in any one of claims 1 to 6 that has been formed by moulding.
8. An article as claimed in any one of claims 1 to 6 that is in the form of a sleeve. 40
9. An article as claimed in any one of claims 1 to 8 which is dimensionally heat-recoverable.
10. A heat recoverable flame retarded hollow article formed from a composition substantially as described in Examples 1, 2 or 5 herein.